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## COORDINATION PROPERTIES OF SOME MIXED AMINO ACID METAL COMPLEXES

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#### ABSTRACT

A series of mixed-ligand complexes of the formulae [Co  $(tyr)(gly)(H_2O)_2$ ], [Co $(tyr)(ala)(H_2O)_2$ ], [Co $(tyr)(thr)(H_2O)_2$ ], [Co $(tyr)(met)(H_2O)_2$ ], [Ni $(tyr)(gly)(H_2O)_2$ ], [Ni $(tyr)(ala)(H_2O)_2$ ] and [Ni $(tyr)(thr)(H_2O)_2$ ], where tyr = L-tyrosine, gly = glycine, ala = alanine, thr = threonine, met = L-methionine has been prepared and characterised on the basis of elemental analyses, spectroscopic, thermal analysis and X-ray powder diffraction data. An octahedral structure has been proposed for all of the prepared complexes. The thermal behaviour of the complexes has been studied before and after  $\gamma$ -irradiation.

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#### **INTRODUCTION**

Mixed-ligand complexes are known to play an important role in biological systems<sup>1</sup>, *e.g.* mixed-ligand complexes of acetylacetonate and dithiocarbamate show variable degrees of biological activity against bacteria and fungi<sup>2,3</sup>. There are many reports in the literature on mixed-ligand complexes of amino acids. Srivastava and Gupta *et al.*<sup>4–7</sup> reported the synthesis and characterisation of mixed-ligand transition metal complexes formed with glycine, alanine, uracil, 2-thiouracil, thymine, adenine, histidine, valine and leucine. Grecu and Saxena *et al.*<sup>8,9</sup> also prepared mixed-ligand amino acid complexes of transition and non-transition metals involving the amino acids aspartic acid, glutamic acid and methionine. Structural studies of many transition metal complexes showed that the amino acids coordinate in various ways, depending upon the metal ion, its oxidation state and the primary structure of the amino acid in question<sup>10</sup>

Furthermore, thermal analysis methods play an important role in studying the structures and properties of metal complexes. They were applied to determine the thermal stability ranges, the thermal character of the decomposition processes and the stoichiometry of the decomposition products. The present work describes the preparation and characterisation of some mixed-ligand complexes of Co(II) and Ni(II) containing tyrosine, glycine, alanine, methionine or threonine (Fig. 1). The thermal decomposition characteristics of the complexes were also studied.

NH2CH2COOH

glycine (gly)

CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>CHNH<sub>2</sub>COOH

methionine (met)

CH2CHNH2COOH HO L-tyrosine (tyr)

CH<sub>2</sub>CHNH<sub>2</sub>COOH

alanine (ala)

#### CH<sub>3</sub>CH(OH)CHNH<sub>2</sub>COOH

threonine (thr)

Figure 1. Structures of the amino acid ligands.

#### EXPERIMENTAL

All chemicals were of analytical grades. Glycine (BDH), alanine (GPR), methionine (BDH), threonine (BDH), and tyrosine (BDH) were used as such. Sodium salt solutions of the amino acids were prepared by adding sodium hydroxide solution (0.1 N) to an aqueous amino acid solutions in stoichiometric ratio.

The preparation of Co(II) and Ni(II) mixed-ligand complexes followed essentially the same procedure. The preparation of the (tyrosinato) (glycinato)cobalt(II) complex is typical.

An aqueous solution (10 mL) of cobalt chloride hexahydrate (1.00 g, 4 mmol) was added to a stirred solution of tyrosine (0.72 g, 4 mmol) in 0.1 N NaOH solution (20 mL), followed by the addition of an aqueous solution (10 mL) of glycine (0.30 g, 4 mmol). The pH value was adjusted to 6–7 by adding NaOH solution (0.1 N). The mixture was then refluxed for about one hour and then concentrated whereupon a pale green product precipitated which was filtered off, washed with water and dried over  $P_4O_{10}$ ; yield 1.1 g.

#### **Physical Measurements**

The infrared spectra were obtained in the solid state (KBr pellets) on a 470 Shimadzu infrared spectrophotometer. Electronic spectra were recorded in DMF on a UV-2101 PC Shimadzu spectrophotometer. The thermogravimetric analyses were determined using an electrobalance of the type Sartorius 200 MP converted to a thermobalance by the addition of a small furnace and sample holder. The temperature was measured using a Chromal-Alumal thermocouple attached to a type Soor MF 550 digital multimeter; the heating rate was 8 °C min<sup>-1</sup>. The X-ray powder diffractometer was a Philips 1700 version with H.TPW 1370/10, 4 KVA CuK<sub>α</sub> $\lambda$  = 1.54180 Å.

For gamma irradiation a type AlyconII Co-60 instrument was used. The samples were kept in small glass containers and irradiated for appropriate irradiation times at ambient temperature using a <sup>60</sup>Co gamma cell having a dose rate of 1.1 Gy/s.

#### **RESULTS AND DISCUSSION**

To establish the composition of the coordination compounds, the percent composition of carbon, hydrogen, nitrogen and metal were deter-

Complex		F	ound (	Calcd.%	<b>(</b> 0)		
(Empirical Formula) (Formula Weight)	Colour	С	Ν	Н	М	Yield. %	M.p. (°C) (Decomp.)
$[Co(tyr)(gly)(H_2O)_2]$	Pink	37.49	8.24	5.30	17.12	75	305
$(C_{11}H_{19}N_2O_7C_0)$ (349.01)		(37.83)	(8.02)	(5.19)	(16.87)		
$[Co(tyr)(ala)(H_2O)_2]$	Pink	40.24	7.59	5.50	16.10	72	299
$(C_{12}H_{21}N_2O_7Co)$ (363.05)		(39.68)	(7.71)	(5.55)	(16.22)		
$[Co(tyr)(thr)(H_2O)_2]$	Pink	40.03	7.11	5.52	15.10	69	295
$(C_{13}H_{23}N_2O_8Co)$ (393.06)		(39.70)	(7.12)	(5.64)	(14.98)		
$[Co(tyr)(met)(H_2O)_2]$	Pink	39.66	6.60	5.67	14.00	80	300
$(C_{14}H_{25}N_2O_7Co)$ (423.10)		(39.72)	(6.61)	(5.71)	(13.92)		
$[Ni(tyr)(gly)(H_2O)_2]$	Pale	37.70	7.92	5.12	19.90	79	315
$(C_{11}H_{19}N_2O_7Ni)$ (348.76)	green	(37.86)	(8.02)	(5.15)	(16.82)		
[Ni(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	Pale	39.98	7.61	5.56	15.90	67	302
$(C_{12}H_{21}N_2O_7Ni)$ (362.78)	green	(39.70)	(7.71)	(5.55)	(16.17)		
$[Ni(tyr)(thr)(H_2O)_2]$	Pale	40.00	7.12	5.60	15.61	68	299
$(C_{13}H_{23}N_2O_8Ni)$ (392.80)	green	(39.72)	(7.13)	(5.64)	(14.94)		

Table I. Colours, Elemental Analyses, and Melting Points of the Complexes

mined. The results are listed in Table I. The mixed-ligand complexes were prepared according to the following general equation:

$$Htyr + M^{+2} + Haa \xrightarrow{2H_2O} [M(tyr)(aa)(H_2O)_2] + 2H^+$$

where M = Co(II) or Ni(II); Htyr = L-tyrosine; Haa = glycine (gly), alanine (ala), threonine (thr) or L-methionine (met).

The complexes are soluble in DMSO and DMF, but not soluble in most common organic solvents.

#### **IR Spectra**

The IR spectra of the complexes present the characteristic bands of the amino acids involved (Table II). The free amino acids tyrosine, glycine, alanine, threonine and methionine exhibit  $v(NH_2)$  in the range 3265–3300 cm<sup>-1</sup>,  $v_s(COO^-)$  and  $v_{as}(COO^-)$  at 1400–1420 and 1600–1630 cm<sup>-1</sup>, respectively. For the mixed-ligand complexes the stretching vibration of  $v_s(COO^-)$  and  $v_{as}(COO^-)$  appear in the range 1400–1405 cm<sup>-1</sup> and 1570–1598 cm<sup>-1</sup>, respectively. It is to be noted that for all of the studied mixed amino acid complexes,  $v_{as}(COO^-)$  appears as a band associated with a shoulder, indicating the presence of two different amino acids. The com-

Complex	$v_{s}(COO^{-1})$	) $v_{as}(COO^{-1})$	) v(NH	2) v(OH)	(H <sub>2</sub> O) v(M-O)	v(M-N)
$[Co(tyr)(gly)(H_2O)_2]$	1400 m	1595 s, 157	0 w 3250	m 3300	m 495 m	415 w
[Co(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	1402 m	1595 s, 157	5 w 3270	m 3250	m 495 m	412 w
$[Co(tyr)(thr)(H_2O)_2]$	1403 m	1595 s, 157	0 w 3270	m 3400	m 495 m	412 w
[Co(tyr)(met)(H <sub>2</sub> O) <sub>2</sub> ]	1400 m	1595 s, 158	0 w 3270	m 3220	m 495 m	420 w
$[Ni(tyr)(gly)(H_2O)_2]$	1405 m	1597 s, 157	5 w 3280	m 3300	m 495 m	415 w
[Ni(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	1400 m	1598 s, 157	5 w 3280	m 3240	m 495 m	415 w
[Ni(tyr)(thr)(H <sub>2</sub> O) <sub>2</sub> ]	1405 m	1598 s, 157	0 w 3280	m 3200	m 491 m	420 w

*Table II.* IR Spectral Data of the Complexes  $(cm^{-1})$ 

Key: s (strong), m (medium), w (weak).

plexes further display a band in the range  $3250-3280 \text{ cm}^{-1}$  attributed to  $v(\text{NH}_2)$ , typical of coordinated amino groups<sup>4</sup>. Metal-nitrogen and metaloxygen bonding are manifested by the appearance of two bands at 412–  $420 \text{ cm}^{-1}$  and  $491-495 \text{ cm}^{-1}$ , respectively. The OH stretching vibrations of coordinated water are located in the range  $3200-3400 \text{ cm}^{-1}$ . No free carboxylic (COOH) groups could be detected from the IR spectral data, indicating coordination of all of the studied metal ions to the carboxylate anions.

From the foregoing band positions of  $v(NH_2)$ ,  $v(COO^-)$ , v(M-O) and v(M-N) and comparison with similar compounds<sup>4</sup>, it may be concluded that the involved amino acids in the complexes are bidentate coordinating through the  $-NH_2$  and  $COO^-$  groups.

#### **Electronic Spectra**

The electronic spectral data of the complexes were recorded in DMF and are tabulated in Table III. The electronic spectra of both the Co(II) and Ni(II) complexes display d-d transition bands typical of octahedral structures. Thus, the complexes  $[Co(tyr)(gly)(H_2O)_2]$ ,  $[Co(tyr)(ala)(H_2O)_2]$ ,  $[Co(tyr)(thr)(H_2O)_2]$  and  $[Co(tyr)(met)(H_2O)_2]$  exhibit a d-d band in the range 18,622–20,000 cm<sup>-1</sup> corresponding to the transition  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)$  $(\upsilon_3)$ . For the two Ni(II) complexes,  $[Ni(tyr)(ala)(H_2O)_2]$  and [Ni(tyr) $(thr)(H_2O)_2]$ , the d-d band appearing at 16,339–19,305 cm<sup>-1</sup> is ascribed to the transition  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$   $(\upsilon_2)$ . The complex  $[Ni(tyr)(gly)(H_2O)_2]$ , however, displays a d-d transition at 27,322 cm<sup>-1</sup>, attributed to the transition  ${}^{3}A_{1g} \rightarrow {}^{3}T_{1g}(P)(\upsilon_3)$ .

From the foregoing data the structure of the complexes can be postulated as follows (Fig. 2):

Complex	$v_{max} (cm^{-1}),$ ( $\varepsilon_{max}$ ) (M <sup>-1</sup> cm <sup>-1</sup> )	Assignment
$[Co(tyr)(gly)(H_2O)_2]$	19,230 (790)	${}^{4}T_{1\sigma} \rightarrow {}^{4}T_{1\sigma}$ (P)
	36,364 (21772)	intraligand transition
	38,461 (23890)	intraligand transition
$[Co(tyr)(ala)(H_2O)_2]$	18,622 (750)	${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}$ (P)
	36,900 (20995)	intraligand transition
	38,461 (22872)	intraligand transition
$[Co(tyr)(thr)(H_2O)_2]$	19,305 (822)	${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}$ (P)
	36,900 (23450)	intraligand transition
	38,759 (25467)	intraligand transition
$[Co(tyr)(met)(H_2O)_2]$	20,000 (650)	${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}$ (P)
	37,037 (19890)	intraligand transition
	38,759 (21662)	intraligand transition
$[Ni(tyr)(gly)(H_2O)_2]$	27,322 (970)	${}^{3}A_{1g} \rightarrow {}^{3}T_{1g}$ (P)
	34,246 (18998)	intraligand transition
	35,714 (20113)	intraligand transition
$[Ni(tyr)(ala)(H_2O)_2]$	16,339 (935)	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P)
	35,739 (20035)	intraligand transition
	37,037 (21045)	intraligand transition
$[Ni(tyr)(thr)(H_2O)_2]$	19,305 (889)	${}^{3}\text{A2g} \rightarrow {}^{3}\text{T}_{1g}$ (P)
	36,900 (23980)	intraligand transition
	38,461 (25667)	intraligand transition

Table III. Electronic Spectral Data of the Complexes



where R = H,  $CH_3$ ,  $CH_3SCH_2CH_2$ ,  $CH_3CHOH$ *Figure 2.* Structure of the complexes.

Complex	Step	$T_{i}$	T <sub>m</sub>	$T_{\rm f}$	Wt. Loss %
$[Co(tyr)(gly)(H_2O)_2]$	1st	75	130	179	11.12
	2nd	244	350	389	57.00
	3rd	417	433	459	13.23
$[Co(tyr)(ala)(H_2O)_2]$	1st	114	131	197	10.50
	2nd	250	339	422	70.00
$[Co(tyr)(thr)(H_2O)_2]$	1st	103	139	172	9.40
	2nd	261	339	414	74.00
$[Co(tyr)(met)(H_2O)_2]$	1st	100	156	211	9.02
	2nd	281	367	453	69.00
$[Ni(tyr)(gly)(H_2O)_2]$	1st	100	144	186	10.56
	2nd	249	353	403	58.00
	3rd	433	442	464	12.50
[Ni(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	1st	92	117	147	10.00
	2nd	269	350	431	71.00
$[Ni(tyr)(thr)(H_2O)_2]$	1st	111	139	167	9.62
	2nd	271	353	444	70.00

Table IV. Thermal Data of the Complexes

 $T_i$  = initial temperature,  $T_m$  = maximum temperature, and  $T_f$  = final temperature.

#### **Thermal Studies**

The TG and DTG data are presented in Table IV. The TG thermograms of [Co(tyr)(gly)(H<sub>2</sub>O)<sub>2</sub>] and [Ni(tyr)(gly)(H<sub>2</sub>O)<sub>2</sub>] show the same decomposition profiles. These compounds decompose in three steps in the ranges 130-144, 350-353 and 434-442 °C (DTG curves). The first step corresponds to the loss of the two water molecules, the second step is a major step in the TG curve of the two complexes (weight loss of 57.2% for the cobalt complex and 58.0% of the nickel complex) which corresponds to the decomposition of most of the organic moieties. For the complexes  $[Co(tyr)(ala)(H_2O)_2]$ ,  $[Co(tyr)(thr)(H_2O)_2]$ ,  $[Co(tyr)(met)(H_2O)_2]$ , [Ni(tyr) $(ala)(H_2O)_2$  and  $[Ni(tyr)(thr)(H_2O)_2]$  the pyrolysis curves exhibit almost the same TG pattern, namely two decomposition steps in the ranges 117-156 ° and 339-367 °C.

For all of the complexes the final products are the metal oxides (deduced from the TG curves and IR spectra<sup>11</sup>: CoO at 560 and 660 cm<sup>-1</sup>, NiO at 590 and 690 cm<sup>-1</sup>. For the complexes [Co(tyr)(gly)(H<sub>2</sub>O)<sub>2</sub>] and [Ni(tyr)(gly(H<sub>2</sub>O)<sub>2</sub>] the third step corresponds to the metal carbonate, which decomposes to the metal oxide. It seems that the glycinato mixed- ligand complexes possess higher stability than the other amino acids mixed-ligand

complexes. This fact has been reported previoulsy in the literature<sup>12</sup> where mixed-ligand complexes of glycine in solution display the greatest stability.

The Coats-Redfern and Horowitz-Metzger equations were used for evaluating the kinetic parameters<sup>13,14</sup>.

(a) Coats-Redfern equation

$$n\left[\frac{1-(1-\alpha)^{l-n}}{(1-n)T^2}\right] = M/T + B \quad \text{for } n \neq 1$$
(1)

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = M/T + B \quad \text{for } n = 1$$
<sup>(2)</sup>

where M = -E/R and  $B = \ln ZR/\varphi E$ ; E, R, Z and  $\varphi$  are the activation energy, gas constant, pre-exponential factor and heating rate, respectively.

(b) Horowitz-Metzger equation

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\frac{ZRT_s^2}{\phi E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad \text{for } n \neq 1$$
(3)

$$\ln[-\ln(1-\alpha)] = \frac{E\theta}{RT_s^2} \quad \text{for } n = 1 \tag{4}$$

where  $\theta = T - T_s$ ;  $T_s$  is the temperature at the DTG peak.

The correlation coefficient r is computed using the least square method for equations (1), (2), (3) and (4). Linear curves were drawn for different values of n ranging from 0 to 2, in increments of 0.2. The value of n which gave the best fit was chosen as the order parameter for the decomposition stage of interest. The kinetic parameters were calculated from the plots of the left hand side of equations (1) and (2) against 1/T and against  $\theta$  for equations (3) and (4) (Figs. 3 and 4).

A perusal of Table V shows that the activation energy for the dehydration step of the complexes lies in the range 79.0–108.2 kJ/mole. These values are comparable to the generally accepted values of activation energy for coordinated water<sup>15,16</sup>.

#### Thermal Studies of Irradiated Samples

Four complexes were selected for irradiation with  $\gamma$ -rays at doses of  $1 \times 10^3$ ,  $1 \times 10^4$  and  $1 \times 10^5$  Gy. These complexes were [Co(tyr)(gly)(H<sub>2</sub>O)<sub>2</sub>], [Co(tyr)(met)(H<sub>2</sub>O)<sub>2</sub>], [Ni(tyr)(gly)(H<sub>2</sub>O)<sub>2</sub>] and [Ni(tyr)(ala)(H<sub>2</sub>O)<sub>2</sub>].

The irradiated complexes exhibit essentially the same TG pattern as those before irradiation (Table VI). However, irradiation of the complexes

1



*Figure 3.* Horowitz-Metzger plots for the three decomposition steps of [Co(tyr) (gly)H<sub>2</sub>O)<sub>2</sub>] a) first step, b) second step, c) third step; where  $Y = \ln[1 - (1 - \alpha)^{1 - n}/(1 - n)]$  for  $n \neq 1$  or  $Y = \ln[-\ln(1 - \alpha)]$  for n = 1.

produces a profound effect on the TG temperature of decomposition. The Co(II) complexes are more affected than the Ni(II) complexes, which may suggest their lower stability and/or due to the autocatalytic effect of Co(II) on the decomposition of its complexes.



*Figure 4.* Coats-Redfern plots for the three decomposition steps of [Ni(tyr) (gly)H<sub>2</sub>O)<sub>2</sub>] a) first step, b) second step, c) third step; where  $Y = ln[1 - (1 - \alpha)^{1 - n}/(1 - n)T^2]$  for  $n \neq 1$  or  $Y = ln[-ln(1 - \alpha)/T^2]$  for n = 1.

		(	Coats-Red	lfern	Horowitz		z-Metzger	
Complex	Step	n	r	Е	n	r	Е	
$[Co(tyr)(gly)(H_2O)_2]$	1st	1.00	0.9998	86.776	1.00	0.9996	_	
	2nd	2.00	0.9827	125.818	2.00	0.9900	130.720	
	3rd	0.00	0.9880	229.900	0.00	1.000	220.920	
[Co(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	1st	1.00	1.0000	102.880	1.00	0.9996	100.720	
	2nd	2.00	0.9827	107.840	2.00	0.9900	113.600	
$[Co(tyr)(thr)(H_2O)_2]$	1st	1.00	0.9970	_	1.00	0.9990	92.700	
	2nd	1.00	0.9800	63.420	1.00	0.9970	71.060	
$[Co(tyr)(met)(H_2O)_2]$	1st	1.00	0.9970	87.160	1.00	0.9980	91.480	
	2nd	1.00	0.9990	66.790	1.00	1.0000	71.060	
[Ni(tyr)(gly)(H <sub>2</sub> O) <sub>2</sub> ]	1st	1.00	0.9750	79.000	1.00	0.9800	86.250	
	2nd	2.00	0.9980	125.600	2.00	0.9992	131.000	
	3rd	0.00	0.9997	225.000	0.00	1.0000	228.000	
[Ni(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	1st	1.00	0.9987	91.380	1.00	0.9980	92.800	
	2nd	2.00	0.9967	96.140	2.00	0.9963	102.860	
[Ni(tyr)(thr)(H <sub>2</sub> O) <sub>2</sub> ]	1st	1.00	0.9854	108.200	1.00	0.9992	101.770	
	2nd	1.00	0.9937	165.600	1.00	0.9978	169.800	

Table V. Kinetic Parameters of the Thermal Decomposition of the Complexes

E in kJ mol<sup>-1</sup>.

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Table VI. Thermal Data of Irradiated Complexes at Irradiation Doses  $1\times10^3,$   $1\times10^4,$   $1\times10^5~Gy^a$ 

		Irradiation dose $1 \times 10^3$ Gy		Irradiation dose $1 \times 10^4$ Gy			Irradiation dose $1 \times 10^5$ Gy			
Complexes	Step	$T_i$	$T_m$	$T_{\rm f}$	$T_i$	$T_{m}$	$T_{\rm f}$	$T_i$	$T_{m}$	$T_{\rm f}$
$[Co(tyr)(gly)(H_2O)_2]$	1st	74	128	179	74	125	175	68	119	167
	2nd	244	246	387	240	239	380	238	333	374
	3rd	415	429	454	410	420	450	404	410	440
$[Co(tyr)(met)(H_2O)_2]$	1st	94	150	172	90	143	168	81	132	159
	2nd	276	360	445	260	353	439	246	339	437
$[Ni(tyr)(gly)(H_2O)_2]$	1st	98	142	186	98	140	184	94	133	181
	2nd	240	355	399	237	351	396	232	345	390
	3rd	430	438	460	428	435	456	422	430	450
[Ni(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	1st	90	115	146	88	112	144	80	105	140
	2nd	267	345	428	265	340	426	260	331	412

 $^{a}Gy = gray.$ 

*Table VII.* Kinetic Parameters of the Decomposition of the Complexes After Irradiation with  $1 \times 10^3$ ,  $1 \times 10^4$  and  $1 \times 10^5$  Gy Irradiation Doses<sup>a</sup>

		Coa	ats-Red	fern Equ	uation	Horowitz-MetzgerEquatic			
Complex	Step	n	$E_1$	$E_2$	$E_3$	n	$E_1$	$E_2$	$E_3$
$[Co(tyr)(gly)(H_2O)_2]$	1st	1.00	84.24	81.90	80.20	1.00	78.22	74.70	72.98
	2nd	2.00	123.32	121.40	120.02	2.00	127.40	124.30	122.8
	3rd	0.00	225.10	221.70	219.70	0.00	218.12	215.21	213.71
$[Co(tyr)(met)(H_2O)_2]$	1st	1.00	81.34	80.02	79.00	1.00	82.90	81.12	80.02
	2nd	1.00	60.82	57.30	55.32	1.00	61.81	59.14	57.98
$[Ni(tyr)(gly)(H_2O)_2]$	1st	1.00	77.82	76.50	76.04	1.00	84.26	83.17	81.40
	2nd	2.00	123.98	122.71	121.92	2.00	129.00	127.20	125.99
	3rd	0.00	242.72	223.97	223.06	0.00	227.20	226.00	224.72
[Ni(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	1st	1.00	90.02	88.87	87.12	1.00	90.72	88.67	87.06
	2nd	2.00	92.12	94.04	92.97	2.00	101.21	100.17	98.96

 $^a$  E in kJ mol  $^{-1},$  E1 at  $1\times10^3$  Gy, E2 at  $1\times10^4$  Gy and E3 at  $1\times10^5$  Gy.

Table VII includes the initial temperature ( $T_i$ ), peak temperature ( $T_m$ ) and final temperature ( $T_f$ ) of decomposition after irradiation. [Co(tyr) (met)(H<sub>2</sub>O)<sub>2</sub>] is the compound most affected by the three  $\gamma$ -ray doses among the studied complexes. Thus, irradiation lowers  $T_m$  by 6, 13 and 24 °C for the first step and by 7, 14 and 28 °C for the second step upon irradiation with  $1 \times 10^3$ ,  $1 \times 10^4$  and  $1 \times 10^5$  Gy, respectively.

The activation energy for the different decomposition steps was calculated using the Coats-Redfern and Horowitz-Metzger equations. Table VII shows that the activation energy of the irradiated complexes decreases relative to the non-irradiated ones. The two Co(II) complexes display a greater decrease in activation energy than the Ni(II) complexes.

However, there are relatively small changes in activation energy for all of the studied complexes on increasing the radiation dose, suggesting that the same chemical processes govern the decomposition of the complexes for the three doses. The influence of  $\gamma$ -irradiation on the thermal decomposition of [Co(tyr)(met)(H<sub>2</sub>O)<sub>2</sub>] is depicted in Fig. 5.

Inspection of the IR spectra of the irradiated complexes (Fig. 6) shows that the intensity of most bands decreases. However, the position of all the bands did not change with irradiation. Because the intensity of an infrared absorption band depends on the magnitude of the change in electric dipole moment of the bond during the vibrational displacement, it seems that irradiation of the complexes with  $\gamma$ -rays affects only the metal-



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*Figure 5.* TG and DTG thermograms of unirradiated (——) and after  $\gamma$ -irradiation (- - - -) [Co(tyr)(met)(H<sub>2</sub>O)<sub>2</sub>]. Irradiation dose = 1 × 10<sup>5</sup> Gy.



*Figure 6.* IR Spectrum of non-irradiated (\_\_\_\_\_) and after  $\gamma$ -irradiation (----) [Co(tyr)(met)H<sub>2</sub>O)<sub>2</sub>]. Irradiation dose =  $6 \times 10^5$  Gy.

#### MIXED AMINO ACID METAL COMPLEXES

oxygen  $(491-495 \text{ cm}^{-1})$  or metal-nitrogen  $(415-421 \text{ cm}^{-1})$  bond dipole moments and there are really no degradation reactions. As expected from the thermal decomposition data of the Co(II) and Ni(II) complexes, the effect of irradiation on the IR spectra of Co(II) complexes is more profound.

The X-ray powder diffraction patterns of three of the complexes,  $[Co(tyr)(gly)(H_2O)_2]$ ,  $[Co(tyr)(met)(H_2O)_2]$  and  $[Ni(tyr)(gly)(H_2O)_2]$ , besides that of the Co(II)tyrosinate, were recorded. The crystal lattice parameters were computed with the aid of the computer programs TREOR and ITO. Actually, the TREOR program failed to give the best crystal data, while the ITO program was more successful. The latter program is known to be efficient for indexing low-symmetry crystal systems<sup>17</sup>. The crystal data (Table VIII) of the Co(II)tyrosinate and the three mixed-ligand complexes show variable crystal systems ranging from monoclinic to triclinic. This may confirm the formation of the mixed-ligand complexes and exclude the presence of a mixture of two binary complexes.

#### Thin-Layer Chromatography (TLC)

TLC was used for the investigation of  $[Co(tyr)(gly)(H_2O)_2]$ ,  $[Co(tyr)(met)(H_2O)_2]$ ,  $[Ni(tyr)(gly)(H_2O)_2]$  and  $[Ni(tyr)(ala)(H_2O)_2]$  on silica gel and the chromatograms were developed using a DMF-benzene mixture (2:1). Examination of the four complexes under UV light revealed the presence of only one spot with  $R_f$  values 0.74, 0.61, 0.42 and 0.54, respectively. This indicates that pure mixed-ligand complexes were formed. It is to be noted that also one spot with an  $R_f$  value 0.69 was observed for the binary Co(II)tyrosinate,  $[Co(tyr)_2]$ , complex.

#### **Microbiological Screening**

Tests were directed towards bacteria. The bacteria tested were *B. cereus* G+ve, *E. coli* G-ve and *P. aeruginosa* G-ve. The culture media used were nutrient agar (N.A.) media supplemented with one g yeast/liter. The antimicrobial activity of each compound was evaluated by the classical filter paper disc technique<sup>18</sup>.

It is suggested that the neutral ternary complex penetrates the cell and at the site active may undergo dissociation into the corresponding 1:1 binary complexes as shown below:

$$2[M(tyr)(aa)(H_2O)_2] \rightleftharpoons M(tyr)^+ + M(aa)^+ + aa^- + tyr^- + 4H_2O$$

		Ta	ble VIII.	The Crys	stal Data c	f the Com	plexes	
Complex	a (Å)	b (Å)	c (Å)	α	β	λ	Volume of Unit Cell (Å)	Crystal System
$[Co(tyr)_2]$	12.90	14.05	12.30	103.50	100.29	108.31	1980.8	triclinic
$[Co(tyr)(gly)(H_2O)_2]$	11.55	15.74	8.67	98.72	108.52	69.95	1444.8	triclinic
$[Co(tyr)(met)(H_2O)_2]$	17.39	10.53	5.99	90.00	91.50	90.00	2359.6	monoclinic
$[Ni(tyr)(gly)(H_2O)_2]$	18.24	10.71	10.87	90.00	105.78	90.00	2044.8	monoclinic

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Complex	<i>B. cereus</i> G+ve	<i>E. coli</i> G–ve	P. aeruginosa G–ve
$[Co(tyr)(gly)(H_2O)_2]$	_	+	++
$[Co(tyr)(met)(H_2O)_2]$	_	_	+
$[Ni(tyr)(gly)(H_2O)_2]$	_	+	++
[Ni(tyr)(ala)(H <sub>2</sub> O) <sub>2</sub> ]	_	++	-

Table IX. Microbiological Screening of the Complexes

The diameter (D) of the inhibition zone (in mm) is expressed as "+" and "-" "++" D = 15-20 "+" D = 1-15 "-" D = 0.

where M = Co(II) or Ni(II), Haa = glycine, alanine and methionine. Thus, in the mixed-ligand complexes, the two binary complexes,  $M(tyr)^+$  and  $M(aa)^+$ , are acting as toxic agents and the resulting activity is a combination of both. Disproportionation of Co(II) and Ni(II) or the involved amino acids is highly improbable, and therefore we consider only dissociation of the mixed ligand complexes and excluded disproportionation reactions. Furthermore, the complexes may cause disturbance in the respiration process, thus blocking the synthesis of essential components of the cell<sup>3</sup>.

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